Questions and Exercises on Quantum Mechanics

Molecular Modeling of Nanosystems – CNE Master

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1.   The output of a quantum chemistry calculation for the excited states of a molecule is the following.

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Excited State   1:      Singlet-A      3.9661 eV  312.61 nm  f=0.0008  <S**2>=0.000
     44 -> 49         0.48421
     44 -> 53         0.16656
     48 -> 49         0.45653
     48 -> 53         0.14306


Excited State   5:      Singlet-A      5.3101 eV  233.49 nm  f=0.0143  <S**2>=0.000
     44 -> 49        -0.13288
     44 -> 52         0.11442
     45 -> 50        -0.11475
     45 -> 51         0.24448
     46 -> 50        -0.26164
     47 -> 49         0.50829
     48 -> 49         0.12104
     48 -> 52        -0.19407


Excited State   6:      Singlet-A      5.3517 eV  231.67 nm  f=0.0365  <S**2>=0.000
     44 -> 50         0.13327
     45 -> 49         0.43711
     46 -> 49         0.28620
     46 -> 52        -0.23065
     47 -> 50        -0.12128
     47 -> 51         0.25270
     48 -> 50        -0.24286
```

Based on these data, complete the following table.

Excited State	Energy (eV)	Oscillator strength	Main orbital transition
1			
2			
3			

2.   The table below summarizes the energies of the ground singlet state (S_0) and the first excited singlet state (S_1) of a molecule for different nuclear conformations (S_0 minimum, S_1 minimum, and S_0/S_1 intersection). It also shows the oscillator strength between S_0 and S_1. Based on these data
   a) Draw an energy diagram indicating the energy levels as a function of the nuclear geometry.
   b) What are the absorption and fluorescence energies?
   c) Explain what may happen to this molecule after it is photoexcited.

Geometry	State	Energy (eV)	Oscillator strength
S_0 minimum	S_0	0.00	-
	S_1	3.10	0.2
S_1 minimum	S_0	0.30	-
	S_1	2.50	0.2
S_1/S_0 intersection	S_0	2.70	-
	S_1	2.70	-

3.   A molecular system in the *trans* configuration is photoexcited into the second excited singlet state. The schematic potential energy profile for this system connecting the *trans* and *cis* isomers is illustrated below. Based on this figure, describe the possible deactivation pathways of the system until it relaxes back to the ground state.
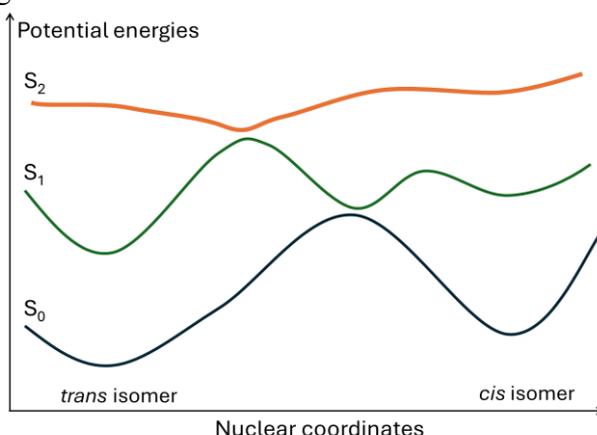
4.   A photoexcited molecular system can get rid of the energy excess from the light absorption via radiative or nonradiative processes.
  a) What is the difference between them?
  b) What are the time scales for each one occurs?
  c) What is a conical intersection, and how does it relate to the relaxation process?

5.   In the time-independent Born-Huang approximation, the nuclear wavefunction χ_n of state n is given by

$$\left(\hat{T}_{nuc} + E_n - \varepsilon\right)\chi_n + \sum_m \hat{N}_{nm}\chi_m = 0$$

where $\hat{T}_{nuc}$ is the nuclear kinetic energy operator, E_n is the electronic potential energy of state n, ε is the molecular energy, $\hat{N}_{nm}$ is the nonadiabatic coupling operator between states n and m, and the summation runs over all states m.
  d) What is the role of $\hat{N}_{nm}$ in this equation?
  e) How can the adiabatic (Born-Oppenheimer) approximation be obtained from this equation?
  f) Write the equation to determine χ_n in the Born-Oppenheimer approximation.

6.   The Born-Oppenheimer molecular wavefunction is

$$\Psi_{BO}\left(\mathbf{r},\mathbf{R}\right) = \chi\left(\mathbf{R}\right)\phi\left(\mathbf{r};\mathbf{R}\right)$$

where $\mathbf{r}$ represents the electronic coordinates, $\mathbf{R}$ represents nuclear coordinates, χ is the nuclear wavefunction, and ϕ is the electronic wavefunction.
  a) What is the rationale behind this approximation? Why can the nuclear and electronic parts be written as a product?
  b) What does the semicolon separating $\mathbf{r}$ and $\mathbf{R}$ mean in the electronic wavefunction?
  c) Born and Huang proposed a more general molecular wavefunction guess. Write it.
  d) Why is the Born-Huang wavefunction a better approximation than the Born-Oppenheimer wavefunction?

7.   Consider the exact molecular wavefunction $\Psi(\mathbf{r}, \mathbf{R})$ or electronic coordinates $\mathbf{r}$ and nuclear coordinates $\mathbf{R}$. What is the simplified wavefunction format that Born and Oppenheimer proposed to simplify $\Psi(\mathbf{r}, \mathbf{R})$?

8.   Under which condition can a nuclear wavepacket be approximated for an ensemble of independent classical copies of the system, as illustrated in the figure?
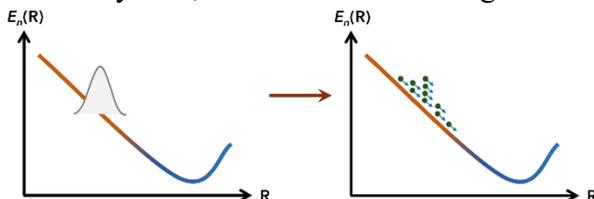
9.   The figure below shows a nuclear wavepacket simulation for CF_3I reported by Yang et al. [*Science*, **2018**, *361*, 6397]. The pair distance represents the C-I distance.
   a) A time zero, what are the most probable C-I distances?
   b) If we make multiple measurements at 600 fs, which C-I distance should we observe? Which is the most likely?
   c) Based on this figure, how do you interpret the branching happening around 200 fs?
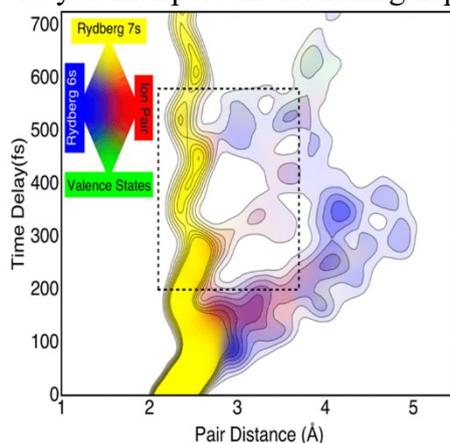
10.   What is quantum decoherence? [This video may help: youtu.be/igsuIuI_HAQ]

11.   Sometimes, we represent a quantum state by the state vector $|\psi\rangle$ and others by the wavefunction $\psi(x)$. What are the differences and the relations between these two concepts?

12.   For a quantum particle with two possible states (*up* and *down*), a possible basis to describe the quantum state is composed of the kets $|up\rangle$ and $|down\rangle$.
   a) What is the dimension of this system's Hilbert space?
   b) If the system contains two of such particles, write a possible basis of kets to describe it. What is the dimension of the Hilbert space?

13.   Consider the state $|\Phi\rangle = \dfrac{1}{\sqrt{2}}\left(|\psi_1\rangle + |\psi_2\rangle\right)$

Give the probability of occurrence of output ψ_1 in an experiment, supposing that $|\psi_1\rangle$ and $|\psi_2\rangle$ form an orthonormal basis.